

PATENT ABSTRACTS OF JAPAN

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(21)Application number : 03-349681 (71)Applicant : NIPPON SHOKUBAI CO LTD
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(54) PRODUCTION OF COATING RESIN

(57)Abstract:

PURPOSE: To provide a coating resin having excellent stability and capable of forming a coating film having excellent waterresistance, coating film hardness, adhesiveness and processability by baking for a short period.

CONSTITUTION: The objective coating resin having a number-average molecular weight of 3,000-50,000 is produced by copolymerizing (a) 1-25wt.% of a polymerizable monomer containing acidic functional group provided that 0.1-10wt.% is a polymerizable monomer containing phosphoric acid group, (b) 0-20wt.% of a polymerizable monomer containing hydroxyl group and (c) 55-99wt.% of other polymerizable monomer in the presence of an aromatic epoxy resin.

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 TI Manufacture of epoxy resin-grafted acrylic copolymers for coatings
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 PA Nippon Catalytic Chem Ind, Japan
 SO Jpn. Kokai Tokkyo Koho, 6 pp.
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 DT Patent
 LA Japanese
 IC ICM C09D151-08
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CLASS

| PATENT NO. | CLASS | PATENT FAMILY CLASSIFICATION CODES |
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| JP 05156204 | ICM | C09D151-08 |
| | ICS | C08F002-44; C08F283-10; C09D163-00 |
| | IPCI | C09D0151-08 [ICM,5]; C08F0002-44 [ICS,5]; C08F0283-10 [ICS,5]; C08F0283-00 [ICS,5,C*]; C09D0163-00 [ICS,5] |

AB The title resins with Mn 3000-50,000, for water-resistant baked paint precoat metals, are manufactured by copolymg. (a) 1-25% acidic functional group-containing monomers containing 0.1-10% (based on total amts.) phosphate group-containing monomers, (b) 0-20% OH-containing monomers, and (c) 55-99% other

monomers in the presence of aromatic epoxy resins. (Thus) 160.5 parts 60%-solid mixture with M 5000 containing 25:4:6:5:25:27:7.8:0.2 Epikote 1001-acryloyloxyethyl acid phosphate-methacrylic acid-hydroxyethyl acrylate-styrene-Et acrylate-Bu acrylate-dimethylaminoethyl methacrylate graft copolymer, 15.5 parts Cymel 303, 0.2 part amine-blocked p-toluenesulfonic acid, and 23.8 parts butyl Cellosolve were mixed, coated on a Zn phosphate-treated steel plate, and baked at 230° for 1 min to give a coating with flexibility, pencil hardness 5H (JIS K 5400), cross-cut adhesion 100/100, and no blistering after 7 days in water or 2 h in boiling water.

ST acrylic copolymer grafted epoxy resin; water resistance epoxy resin coating; flexibility grafted epoxy resin coating; hardness grafted epoxy resin coating; aminoplast acrylic epoxy resin coating

IT Epoxy resins, uses

RL: TEM (Technical or engineered material use); USES (Uses)
 (acrylic-aminoplast-, coatings, water-resistant, with flexibility and hardness, for precoat metals)

IT Aminoplasts

RL: TEM (Technical or engineered material use); USES (Uses)
 (acrylic-epoxy, coatings, water-resistant, with flexibility and hardness, for precoat metals)

IT Acrylic polymers, uses

RL: TEM (Technical or engineered material use); USES (Uses)
 (aminoplast-epoxy, coatings, water-resistant, with flexibility and hardness, for precoat metals)

IT 12597-69-2, Steel, uses

RL: USES (Uses)
 (plates, epoxy resin-grafted acrylic copolymer coatings for, with flexibility and water resistance and hardness)

IT 151752-29-3P 151752-30-6P 151752-31-7P

RL: PREP (Preparation)
 (preparation of, coatings, water-resistant, with flexibility and hardness, for precoat metals)

DERWENT-ACC-NO: 1993-232581

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TITLE: Coating resin prodn. excellent in storage stability and coat properties- copolymerisation of polymerisable monomers in the presence of aromatic epoxy! resin

PATENT-ASSIGNEE: JAPAN SYNTHETIC RUBBER CO LTD[JAPS]

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ABSTRACTED-PUB-NO: JP 05156204A

BASIC-ABSTRACT:

New coating resin (number-average molecular wt is 3,000 - 50,000) is produced by copolymerisation of the following polymerisable monomer component, (a), (b) and (c) in the presence of an aromatic epoxy resin. (a) is polymerisable monomer contg. acidic functional group; 1- 25 wt. %; but the polymerisable monomer contg. phosphoric acid gp is 0.1- 10 wt.%. (b) is polymerisable monomer contg. hydroxyl group; 0- 20 wt. % (c) is the other polymerisable monomer; 55 - 99 wt.%.

In the method for prodn of the coating resin, the amt. of the aromatic epoxy resin to be used is 5 - 60 wt.pts. per 100 wt. pts. polymerisable monomer component.

USE/ADVANTAGE - The coating resin produced in this prodn method can be used by baking for a short time. Since the coating resin is obtd. in the form of an incorporated resin by reaction of the aromatic epoxy resin with acrylic polymers having the phosphoric acid gp and the other acidic functional group and hydroxyl group at request, it is excellent in storage stability, and even through the curing time is short time to introduction of the phosphoric acid group, it can form the coat excellent in adherence, hardness, water resistance, processability, etc

TITLE-TERMS: COATING RESIN PRODUCE STORAGE STABILISED COAT PROPERTIES
COPOLYMERISE POLYMERISE MONOMER PRESENCE AROMATIC POLYEPOXIDE RESIN

DERWENT-CLASS: A14 A82 G02

CPI-CODES: A04-A; A05-A01E4; A07-A04A; A12-B01; A12-B01L; G02-A02C; G02-A02D; G02-A02G; G02-A05;

UNLINKED-DERWENT-REGISTRY-NUMBERS: 0304U; 0426U ; 0760U

POLYMER-MULTIPUNCH-CODES-AND-KEY-SERIALS:

* NOTICES *

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1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the manufacture approach of the resin for covering excellent in hardenability, flexibility, and ** (**) aqueousness.

[0002]

[Description of the Prior Art] Since various merits, such as being easy to carry out recovery of a solvent with few losses of the coating at the time of the paint from which the quality which could produce continuously at high speed and was stabilized is acquired, are demonstrated, the precoat metal by which baking finish is carried out before metalworking is produced by the large quantity. Therefore, in this precoat metal field, the demand of printing time amount shortening of the coating for printing is increasing from a productivity drive, saving resources, and a viewpoint of energy saving, and development research of the coating with which the paint film physical properties excellent in short-time printing are acquired is advanced.

[0003] The aminoplast resin of a self-condensation reaction being promoted by the acid curing catalyst used as an object for baking finish is well-known. [many] However, although the attempt in which introduced an acidic group into acrylic resin and it mixed with aminoplast resin was made only by blending a compound with acidic groups, such as a phosphoric-acid radical, into a covering resin constituent since preservation stability got worse, there was a problem that a paint film degree of hardness got worse with acrylic resin.

[0004] For this reason, although aiming at improvement in paint film physical properties by blending an epoxy resin to the acrylic resin containing an acidic group, and using together with aminoplast resin is also carried out, by the blend system, the present condition is that a satisfying thing is not obtained as the stability of a system is bad, or the engine performance of a paint film is inferior by short-time printing even if compatibility is good since there are few epoxy resins with sufficient compatibility with acrylic resin.

[0005]

[Problem(s) to be Solved by the Invention] The purpose of this invention is to offer the resin for covering which can obtain the paint film which has the water resisting property which was excellent in stability and was further excellent in short-time printing, a paint film degree of hardness, adhesion, and workability.

[0006]

[Means for Solving the Problem] The configuration of this invention which could attain the above-mentioned purpose is following (a) under existence of an aromatic series epoxy resin. - (c) It is number average molecular weight 3000-50000 by carrying out copolymerization of the polymerization nature monomer component. It has a summary at the place which obtains the resin for covering.

[0007] (a) Acid functional-group content polymerization nature monomer; It corrects one to 25% of the weight. 0.1 - 10 % of the weight is a phosphoric-acid radical content polymerization nature monomer (b). Hydroxyl-group content polymerization nature monomer; 0 - 20 % of the weight (c) Other

polymerization nature monomers; 55 - 99 % of the weight [0008]

[Function] this invention person etc. found out that the trouble of the defect of the stability in the blend system of the acrylic resin and the epoxy resin which have an acidic group, compatibility, and paint film physical properties could be solved by compounding acrylic resin under existence of a specific epoxy resin.

[0009] This invention is explained to a detail below. As an aromatic series epoxy resin used in this invention, diglycidyl ether mold epoxy resins, such as bisphenol A diglycidyl ether, bisphenol A G beta-methyl-diglycidyl ether, tetrahydroxyphenylmethanetetraglycidyl ether, novolak glycidyl ether, and diglycidyl ether of the bisphenol A alkylene oxide addition product, are mentioned. Although these one sort or two sorts or more can be used, especially a desirable thing is the diglycidyl ether mold epoxy resin of bisphenol A.

[0010] the weight per epoxy equivalent of these aromatic series epoxy resins, and 170-4000 -- it is desirable -- the thing of 200-2000 is used. Weight per epoxy equivalent If fewer than 170, the degree of hardness of the hardening paint film of the constituent after composition may be insufficient, and since viscosity is too high, it becomes an ununiformity and is not desirable [the polymerization of the below-mentioned monomer] at 4000 or more.

[0011] The amount of the above-mentioned aromatic series epoxy resin used is the below-mentioned monomer component 100. As opposed to the weight section 5 - 60 weight section is suitable. It is not desirable in order that the flexibility of a paint film may decrease, if the degree of hardness of the hardening paint film by the epoxy resin and the flexible disposition top effectiveness will not be discovered if fewer than 5 weight sections, and it is used exceeding 60 weight sections.

[0012] Next, a monomer component is explained. (a) which can be used in this invention As an acid functional-group content polymerization nature monomer, a carboxyl group content polymerization nature monomer, a sulfonic group content polymerization nature monomer, and the polymerization nature monomer containing the phosphoric-acid radical contained in indispensable are mentioned. As a carboxyl group content monomer, an acrylic acid (meta), a crotonic acid, an itaconic acid, a maleic acid, a maleic anhydride, etc. are illustrated, and a vinyl sulfonic acid, styrene sulfonic-acid sulfoethyl (meta) acrylate, etc. can be illustrated as a sulfonic group content monomer.

[0013] moreover, as a phosphoric-acid radical content monomer contained in indispensable (meth) acryloyloxy alkyl acid phosphate and the alkylene oxide addition products of those, such as methacryloyloxy-ethyl acid phosphate, (meth)acryloyloxy alkyl acid FOSUFAITO or the alkylene oxide addition product of those, The ester compound of epoxy group content vinyl system monomers, such as glycidyl (meta) acrylate and methyl glycidyl (meta) acrylate, a phosphoric acid, phosphorous acid, or these acid ester etc. is mentioned. One sort chosen from these groups or two sorts or more can be used.

[0014] the above-mentioned phosphoric-acid radical content monomer is blended in order to have the hardening reaction facilitatory effect of aminoplast resin and to raise paint film adhesion further -- having -- the amount used -- (a), (b), and (c) from -- becoming all inside of a polymerization nature monomer component 0.1 - 10 % of the weight -- required -- desirable -- 1-8 It is weight %. If fewer than 0.1 % of the weight, a hardening facilitatory effect and paint film adhesion will not be discovered, and if [than 10 % of the weight] more, it will gel during a polymerization, or the stability when mixing with aminoplast resin and considering as the resin constituent for covering after a polymerization, worsens.

[0015] the monomer which has acid functional groups other than a phosphoric-acid radical -- the inside of a monomer component -- the amount used desirable [0.9 - 15 % of the weight], and more desirable the inside of the monomer which is 5 - 15 % of the weight, and has an aforementioned carboxyl group or an aforementioned sulfonic group -- one sort -- or two or more sorts can be used. These carboxyl groups or a sulfonic group content monomer If the adhesion over a metal runs short if fewer than 0.9 % of the weight, and it is used exceeding 15 % of the weight, since the water resisting property of a paint film gets worse, it is not desirable.

[0016] Hydroxyl-group content polymerization nature monomer (b) If it carries out, hydroxyethyl (meta) acrylate, hydroxypropyl (meta) acrylate, caprolactone denaturation hydroxy (meta) acrylate (for example, Daicel Chemical Industries, Ltd. make; plaque cel FM), the monochrome (meta) acrylate of

the polyester diol obtained from a phthalic acid and propylene glycol, etc. are mentioned, for example. [0017] the above-mentioned hydroxyl-group content monomer (b) the amount used -- inside of the monomer component whole quantity 0 - 20 % of the weight -- more -- desirable -- It is 0 - 10 % of the weight. Since a hydroxyl group generates when the epoxy group of said epoxy resin which exists in indispensable at the time of a polymerization carries out ring breakage, although the hydroxyl group is required for a hardening reaction with aminoplast resin It is 0 - 20 % of the weight. If it exceeds 20 % of the weight, in order that crosslinking density may go up too much, adhesion and flexibility worsen.

[0018] Other polymerization nature monomers (c) If it carries out, methyl (meta) acrylate, Ethyl (meta) acrylate, propyl (meta) acrylate, isopropyl (meta) acrylate, Butyl (meta) acrylate, isobutyl (meta) acrylate, the 3rd class butyl (meta) acrylate, 2-ethylhexyl (meta) acrylate, lauryl (meta) acrylate, Stearyl (meta) acrylate, cyclohexyl (meta) acrylate, Epoxy group content polymerization nature monomers, such as acrylic-acid (meta) alkyl ester; glycidyl (meta) acrylate, such as methylcyclohexyl (meta) acrylate and the 3rd class butyl cyclohexyl (meta) acrylate; (meta) Acrylamide, Methyl alkoxy (meta) acrylamide, N, and N'-dimethylaminoethyl (meta) acrylate, Nitrogen content polymerization nature monomers, such as vinylpyridine and a vinyl imidazole; A vinyl chloride, Halogen content polymerization nature monomers, such as a vinylidene chloride; Styrene, alpha methyl styrene, aromatic series polymerization nature monomers [, such as vinyltoluene,]; -- vinyl ester [, such as vinyl acetate,]; -- vinyl ether; (meta) -- polymerization nature cyanides [, such as acrylonitrile,]; -- glycidyl with 2 and 4-dihydroxy benzophenone or 2, 2', and 4-trihydroxy benzophenone The 2-hydroxy-4-[3-(meta) acrylic oxy--2-hydroxy propoxy] benzophenone reacted and obtained in acrylate, (Meta) Polymerization nature ultraviolet absorption nature monomers, such as a 2 and 2'-dihydroxy-4-[3-(meta) acrylic oxy--2-hydroxy propoxy] benzophenone, etc. are mentioned, and one sort chosen from these groups or two sorts or more can be used.

[0019] Other monomers (c) It is the principal component which is used 55 to 99% of the weight among [all] a polymerization nature monomer component, and determines paint film physical properties. It is desirable to use styrene ten to 40% of the weight among [all monomer] a component from a degree of hardness or a waterproof field.

[0020] In this invention, it describes above under existence of said aromatic series epoxy resin. (a) - (c) Although the polymerization of the monomer component is carried out, a solution polymerization method well-known as a polymerization method is employable. As a solvent which can be used in case a solution polymerization method is adopted, alkylene glycol monoalkyl ether, such as fatty alcohol; ethylene glycol monomethyl ether, such as ketones; isopropanols, such as acetic-ester; methyl ethyl ketones, such as aromatic hydrocarbon; ethyl acetate, such as toluene and a xylene, and butyl acetate, and methyl isobutyl ketone, n-butanol, and an iso-butanol, ethylene glycol monoethyl ether, and diethylene glycol monoethyl ether, can be mentioned.

[0021] Although these solvents can use one sort or two sorts or more, the amount used is the polymerization nature monomer component 100. The 25 sections - the 100 weight sections are suitable to the weight section. Moreover, since it was easy to gel during the polymerization when the phosphoric-acid radical content monomer existed, but it became clear that gelation did not take place when fatty alcohol, such as n-butanol, was contained in the solvent, it is a polymerization nature monomer. It is desirable that more than 10 weight sections consider as fatty alcohol to the 100 weight sections.

[0022] As a polymerization initiator, radical polymerization initiators, such as azobisisobutyronitril, benzoyl peroxide, and the 3rd class butyl peroxide of II, can be mentioned. These polymerization initiators are used in 0.1 - 10% of the weight of the range to the total amount of a polymerization nature monomer component. Reaction temperature is from a room temperature. 200 degrees C is the range of 40 to 140 degree C preferably. Moreover, in case a polymerization reaction is performed, chain transfer agents and modifiers, such as lauryl mercaptan, 2-mercaptoethanol, a carbon tetrachloride, and carbon tetrabromide, may be used in order to adjust molecular weight.

[0023] The resin for covering which consists of denaturation acrylic resin in which the acrylic copolymer with which the aromatic series epoxy resin, the phosphoric-acid radical, the acid functional

group, and the hydroxyl group were introduced carried out the graft, and which reacted with the epoxy group, and it unified by part for a phosphoric-acid base by the above polymerization is compounded. The number average molecular weight of this resin for covering is 3000-50000. It is suitable. When number average molecular weight is smaller than 3000, since the physical properties of the paint film after hardening are inferior, it is 50000 preferably. Since the viscosity of resin becomes high in being large, inconvenience is produced in handling as a coating.

[0024] Although it is also possible to use it independently, as for the resin for covering manufactured by this invention, it is desirable to mix and use aminoplast resin. Moreover, as aminoplast resin, alkyl etherized melamine resin, alkyl ether-ized benzoguanamine resin, an alkyl ether-ized urea-resin, etc. can be mentioned, and one sort or two sorts or more of such mixture can be used, for example. The amount of the aminoplast resin used is resin for covering. As opposed to the 100 weight sections It is good to blend at a rate of 5 - 70 weight section. The amount of the aminoplast resin used Under in 5 weight sections, bridge formation is inadequate, it becomes difficult to obtain a durable paint film, and a water resisting property and a paint film degree of hardness fall. Moreover, since flexibility is inferior when it uses exceeding 70 weight sections, it is not desirable.

[0025] Various additives for coatings, such as the curing catalyst for promoting a reaction, an organic solvent, a bulking agent, a leveling agent, a dispersant, a plasticizer, a stabilizer, a color, and a pigment, can be used for the resin for covering of this invention, blending them suitably.

[0026] As a pigment which can be used for the resin for covering of this invention, in an inorganic pigment, color pigments, such as white pigments, such as titanium oxide, an antimony trioxide, a zinc white, RITOBON, and the white lead, carbon black, the chrome yellow, a molybdate orange, a red oxide, Synthetic Ochre, and Huang Hua, can be mentioned, phthalocyanines, such as azo compounds, such as a benzidine and Hansa yellow, and a copper phthalocyanine blue, can be mentioned in an organic pigment, and these one sort or two sorts or more can be used, for example. Moreover, these pigments are desirable, when choosing a pigment with good weatherability is recommended, for example, a good result is obtained in respect of rather than calling [which uses the titanium oxide of a rutile mold] it the weatherability of a paint film, using the titanium oxide of an anatase as titanium oxide which is white pigments and the direction of chlorine method titanium oxide makes weatherability discover from sulfuric-acid method titanium oxide further over a long period of time so that the weatherability of a paint film may not be reduced.

[0027]

[Effect of the Invention] Since the resin for covering of this invention is resin which the aromatic series epoxy resin reacted with the acrylic copolymer which has a hydroxyl group by the phosphoric-acid radical, other acid functional groups, and request, and was unified, it excels in preservation stability and the setting time can form further the paint film which excelled [workability / adhesion, a degree of hardness, a water resisting property,] also in short ***** by installation of a phosphoric-acid radical.

[0028]

[Example] Although an example is given and this invention is explained concretely hereafter, this invention is not limited to these examples. In addition, "%" and the "section" show "% of the weight" and the "weight section", respectively.

[0029] In 4 opening flask equipped with example of manufacture 1 thermometer, an agitator, nitrogen gas installation tubing, a reflux condenser, and driptank The butyl-cellosolve 26 section, the n-butanol 17 section, and Epicoat 1001 (oil-ized shell epoxy company make; weight per epoxy equivalent 450-500) 25 section preparation, It keeps at 90 degrees C under churning, introducing nitrogen gas, and is acryloyloxyethyl acid phosphate from driptank. The four sections, Methacrylic acid The six sections, hydroxyethyl acrylate The five sections, the styrene 25 section, The ethyl acrylate 27 section, n-butyl acrylate The 7.8 sections, dimethylaminoethyl methacrylate The 0.2 sections, azobisisobutyronitril The mixture of the three sections was dropped over 4 hours. After making it react at 90 degrees C after that for 2 hours, it is azobisisobutyronitril further. 0.3 section addition was carried out, it maintained for 4 hours, and the reaction was ended. The butyl-cellosolve 24 section was added and the resin A1 for covering of 60% of solid content, number average molecular weight 5000, the viscosity of 15000cps (25

degrees C; it is the same a Brookfield viscometer and the following), and the acid number 30 was obtained.

[0030] In 4 opening flask equipped with example of manufacture 2 thermometer, an agitator, nitrogen gas installation tubing, a reflux condenser, and driptank The butyl-cellosolve 50 section, the n-butanol 17 section, Epicoat 1004 (oil-ized shell epoxy company make; weight per epoxy equivalent 900-1000) 15 section preparation, It keeps at 90 degrees C under churning, introducing nitrogen gas, and is methacryloiloxy-ethyl acid phosphate from driptank. The two sections, Methacrylic acid The eight sections, hydroxyethyl acrylate The seven sections, the styrene 30 section, the ethyl acrylate 30 section, n-butyl acrylate The eight sections, azobisisobutyronitril The mixture of the five sections was dropped over 4 hours. After making it react at 90 degrees C after that for 2 hours, it is azobisisobutyronitril further. 0.5 section addition was carried out, it maintained for 3 hours, and the reaction was ended. The resin A2 for covering of 60% of solid content, number average molecular weight 4000, the viscosity of 16000cps, and the acid number 35 was obtained.

[0031] In 4 opening flask equipped with example of manufacture 3 thermometer, an agitator, nitrogen gas installation tubing, a reflux condenser, and driptank The butyl-cellosolve 35 section, n-butanol The eight sections and Epicoat 1001 The 20 sections, Acryloyloxyethyl acid phosphate The four sections are taught. It keeps at 90 degrees C under churning, introducing nitrogen gas, and is a methacrylic acid from driptank. The eight sections, Hydroxyethyl acrylate The five sections, the styrene 25 section, the ethyl acrylate 30 section, n-butyl acrylate The eight sections, azobisisobutyronitril The mixture of the three sections was dropped over 4 hours. After making it react at 90 degrees C after that for 2 hours, it is azobisisobutyronitril further. 0.3 section addition was carried out, it maintained for 4 hours, and the reaction was ended. The butyl-cellosolve 24 section was added and resin A3 for covering of 60% of solid content, number average molecular weight 4000, the viscosity of 18000cps, and the acid number 40 was obtained.

[0032] Resin A4 for covering of 60% of solid content, number average molecular weight 3500, the viscosity of 11000cps, and the acid number 35 was obtained like the example 3 of manufacture except having changed example of manufacture 4 Epicoat 1001 to Epicoat 828 (oil-ized shell epoxy company make; weight per epoxy equivalent 182-194).

[0033] Except having not used example of comparison manufacture 1 Epicoat 1001, the polymerization was performed completely like the example 3 of manufacture, and the resin B1 for covering of 60% of solid content, number average molecular weight 12000, the viscosity of 15000cps, and the acid number 45 was obtained.

[0034] Except having not used Epicoat 1001 for the resin B1 obtained in the example 1 of example of comparison manufacture 2 comparison manufacture 20% of the weight, the polymerization was performed completely like the example 3 of manufacture, and resin B-2 for covering of 60% of solid content, number average molecular weight 12000, the viscosity of 15000cps, and the acid number 45 was obtained.

[0035] Except having not used example of comparison manufacture 3 acryloyloxyethyl acid phosphate, the polymerization was performed completely like the example 3 of manufacture, and the resin B3 for covering of 60% of solid content, number average molecular weight 3500, the viscosity of 15000cps, and the acid number 35 was obtained.

[0036] the resin A160.5 section for example 1 covering, and a hexamethoxy melamine (; by Mitsui Toatsu Chemicals, Inc. Cymel 303; solid content 100%) -- the Para toluenesulfonic acid 0.2 section and the butyl-cellosolve 23.8 section which carried out the amine block were mixed the 15.5 sections, and the coating constituent was created.

[0037] The resin for covering was changed to the appearance shown in one to examples 2-4 and example of comparison 3 table 1, and the coating constituent was created like the example 1.

[0038] the resin 32.0 section for covering and the methyl ether-ized methylol melamine (88% of solid content [Mitsui Toatsu Chemicals, Inc. make; Cymel 370;]) which were shown in five to example 6 table 1 the 9.4 sections and titanium oxide -- Para toluenesulfonic acid which carried out the amine block the 27.5 section The 0.2 sections and the butyl-cellosolve 30.9 section were mixed, and the

coating constituent was created.

[0039] the coating constituent obtained in the example -- thickness coating is carried out using a roll so that the film thickness after drying to a 0.3mm phosphoric-acid zinc processing steel plate may be set to 15-20 micrometers -- printing was performed for 1 minute at 230 degree C. The paint film after printing was evaluated about the following items, and the result was written together to Table 1.

[0040] <Coating stability> Visual observation of thickening when saving for one month at 50 degrees C and the separation condition was carried out.

<Water resisting property> Milkiness of the paint film seven days after underwater immersion and the condition of a blister were visually judged in ordinary temperature.

<Priming-proof nature> Milkiness of the paint film after 2-hour immersion and the condition of a blister were visually judged to the boiling water.

[0041] <Workability> Test piece 180 degrees was bent (OT) and the crack of a flection and the desquamative state were judged visually.

<Shock resistance nature> E. I. du Pont de Nemours 1/2 Inch It carried out in the load of 500 g, and the distance of 50cm, and the crack of a paint film and the desquamative state were judged visually.

<Pencil degree of hardness> JIS S 6006 The pencil specified is used and it is JIS K 5400. It followed and measured.

[0042] <adhesion> -- 1cm² inside -- 1mm width of face 100 measure eyes were made and the number of eyes with which it remained after tape exfoliation was shown.

<salt fog-proof nature> -- the seal of except for a painted surface is carried out, and after cutting until it reaches a paint film side side at a base, it puts into a salt spray test machine -- it took out 500 hours after and tape exfoliation was performed. O and 1-3mm were made into **, and 3mm or more was made into x for single-sided exfoliation width of face of 1mm or less.

[0043]

[Table 1]

| | 実 施 例 | | | | | | 比 較 例 | | |
|--|---|---|---|---|---|---|---|--|--|
| | 1 | 2 | 3 | 4 | 5 | 6 | 1 | 2 | 3 |
| 被覆用樹脂 A1 " A2 " A3 " A4 " B1 " B2 " B3 | 70 | 70 | 70 | 70 | 70 | 70 | 70 | 70 | 70 |
| ヘキサメトキシ メラミン メチロール メチル化メラミン | 30 | 30 | 30 | 30 | 30 | 30 | 30 | 30 | 30 |
| 塗料安定性 耐水性 耐沸水性 加工性 耐衝撃性 鉛筆硬度 密着性 耐塩水噴霧性 | ○ ○ ○ ○ ○ 5H 100 ○ | ○ ○ ○ ○ ○ 5H 100 ○ | ○ ○ ○ ○ ○ 5H 100 ○ | ○ ○ ○ ○ ○ 4H 100 ○ | ○ ○ ○ ○ ○ 5H 100 ○ | ○ ○ ○ ○ ○ 5H 100 ○ | ○ ○ ○ クラック有 剥離 5H 70 △ | 増粘後分離 白化 ブリストア ○ ○ 3H 100 ○ | ○ 化 白 ○ ○ △ 3H 75 △ |

被覆用樹脂とメラミンの配合比は固形分換算である。

[Translation done.]

* NOTICES *

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3. In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1] Under existence of an aromatic series epoxy resin, it is following (a). - (c) It is number average molecular weight 3000-50000 by carrying out copolymerization of the polymerization nature monomer component. The manufacture approach of the resin for covering characterized by obtaining the resin for covering.

(a) Acid functional-group content polymerization nature monomer; It corrects one to 25% of the weight. 0.1 - 10 % of the weight is a phosphoric-acid radical content polymerization nature monomer (b). Hydroxyl-group content polymerization nature monomer; 0 - 20 % of the weight (c) Other polymerization nature monomers; it is [Claim 2] 55 to 99% of the weight. The amount of the above-mentioned aromatic series epoxy resin used receives the above-mentioned polymerization nature monomer component 100 weight section. The manufacture approach of the resin for covering according to claim 1 which is 5 - 60 weight section.

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(54)【発明の名称】 被覆用樹脂の製造方法

(57)【要約】

【目的】 安定性に優れ、さらに短時間の焼付けで優れた耐水性、塗膜硬度、密着性、加工性を有する塗膜を得ることができる被覆用樹脂を提供することにある。

【構成】 芳香族エポキシ樹脂の存在下で、下記(a)～(c)の重合性単量体成分を共重合させることによって数平均分子量3000～50000の被覆用樹脂を得ることを特徴とする被覆用樹脂の製造方法。

(a) 酸性官能基含有重合性単量体；1～25重量%
ただし 0.1～10重量%はリン酸基含有重合性単量体

(b) 水酸基含有重合性単量体；0～20重量%

(c) その他の重合性単量体；55～99重量%

【特許請求の範囲】

【請求項1】 芳香族エポキシ樹脂の存在下で、下記(a)～(c)の重合性単量体成分を共重合させることによって数平均分子量3000～50000の被覆用樹脂を得ることを特徴とする被覆用樹脂の製造方法。

- (a) 酸性官能基含有重合性単量体；1～25重量%
ただし0.1～10重量%はリン酸基含有重合性単量体
(b) 水酸基含有重合性単量体；0～20重量%
(c) その他の重合性単量体；55～99重量%

【請求項2】 上記芳香族エポキシ樹脂の使用量が、上記重合性単量体成分100重量部に対して5～60重量部である請求項1記載の被覆用樹脂の製造方法。

【発明の詳細な説明】

【0001】

【産業上の利用分野】本発明は硬化性、可撓性、耐(湿)水性に優れた被覆用樹脂の製造方法に関するものである。

【0002】

【従来の技術】金属加工前に焼付け塗装されるプレコートメタルは、高速で連続生産が可能である、安定した品質が得られる、塗装時の塗料のロスが少ない、溶剤の回収がし易い等の種々のメリットが発揮されるため多量に生産されている。従ってこのプレコートメタル分野では、生産性向上、省資源、省エネルギーの観点から焼付け用塗料の焼付け時間短縮化の要求が高まっており、短時間の焼付けで優れた塗膜物性が得られる塗料の開発研究が進められている。

【0003】焼付け塗装用として多く用いられるアミノプラスト樹脂は、酸性硬化触媒によって自己縮合反応が促進されることは公知である。しかし、リン酸基等の酸性基を持つ化合物を被覆樹脂組成物中に単に配合するだけでは保存安定性が悪化するため、酸性基をアクリル系樹脂中に導入してアミノプラスト樹脂と混合するという試みがなされたが、アクリル系樹脂によって塗膜硬度が悪化するという問題があった。

【0004】このため酸性基を含有するアクリル樹脂にエポキシ樹脂をブレンドし、アミノプラスト樹脂と併用することによって、塗膜物性の向上を図ることも実施されているが、アクリル樹脂との相溶性が良いエポキシ樹脂が少ないため、系の安定性が悪かったり、あるいは相溶性がよくても短時間焼付けでは塗膜の性能が劣るといように、ブレンド系では満足のいくものが得られないのが現状である。

【0005】

【発明が解決しようとする課題】本発明の目的は、安定性に優れ、さらに短時間の焼付けで優れた耐水性、塗膜硬度、密着性、加工性を有する塗膜を得ることができる被覆用樹脂を提供することにある。

【0006】

【課題を解決するための手段】上記目的を達成し得た本

発明の構成は、芳香族エポキシ樹脂の存在下で、下記(a)～(c)の重合性単量体成分を共重合させることによって数平均分子量3000～50000の被覆用樹脂を得るところに要旨を有する。

【0007】(a) 酸性官能基含有重合性単量体；1～25重量%

ただし0.1～10重量%はリン酸基含有重合性単量体

(b) 水酸基含有重合性単量体；0～20重量%

(c) その他の重合性単量体；55～99重量%

【0008】

【作用】本発明者等は、酸性基を有するアクリル系樹脂とエポキシ樹脂とのブレンド系における安定性、相溶性、および塗膜物性の不良という問題点が、特定のエポキシ樹脂の存在下にアクリル系樹脂の合成を行なうことによって解決できることを見出した。

【0009】以下本発明を詳細に説明する。本発明において用いられる芳香族エポキシ樹脂としては、ビスフェノールAジグリシジルエーテル、ビスフェノールAジ-β-メチル-ジグリシジルエーテル、テトラヒドロキシフェニルメタンテトラグリシジルエーテル、ノボラックグリシジルエーテル、ビスフェノールAアルキレンオキサイド付加物のジグリシジルエーテル等のジグリシジルエーテル型エポキシ樹脂が挙げられる。これらの1種または2種以上を使用することができるが、特に好ましいものは、ビスフェノールAのジグリシジルエーテル型エポキシ樹脂である。

【0010】これらの芳香族エポキシ樹脂のエポキシ当量は、170～4000、好ましくは、200～2000のものが使用される。エポキシ当量が170より少ないと合成後の組成物の硬化塗膜の硬度が不足することがあり、4000以上では、粘度が高すぎるため後述の単量体の重合が不均一になり好ましくない。

【0011】上記芳香族エポキシ樹脂の使用量は、後述の単量体成分100重量部に対して5～60重量部が適している。5重量部より少ないと、エポキシ樹脂による硬化塗膜の硬度および可撓性向上効果が発現せず、また60重量部を超えて使用すると塗膜の可撓性が減少するため好ましくない。

【0012】次に単量体成分について説明する。本発明において用いることができる(a)の酸性官能基含有重合性単量体としては、カルボキシル基含有重合性単量体、スルホン酸基含有重合性単量体、および必須的に含まれるリン酸基を含有する重合性単量体が挙げられる。カルボキシル基含有単量体としては、(メタ)アクリル酸、クロトン酸、イタコン酸、マレイン酸及び無水マレイン酸等が例示され、スルホン酸基含有単量体としてはビニルスルホン酸、スチレンスルホン酸スルホエチル(メタ)アクリレート等を例示できる。

【0013】また必須的に含まれるリン酸基含有単量体としては、メタクリロイルオキシエチルアジドフォス

フェート等の(メタ)アクリロイルオキシアルキルアシッドフォスフェート類またはそのアルキレンオキシド付加物、(メタ)アクリロイルオキシアルキルアシッドフォスファイト類またはそのアルキレンオキシド付加物、グリシジル(メタ)アクリレートやメチルグリシジル(メタ)アクリレート等エポキシ基含有ビニル系モノマーとリン酸または亜リン酸あるいはこれらの酸性エステル類とのエステル化合物等が挙げられ、これらの群から選ばれる1種または2種以上を用いることができる。

【0014】上記リン酸基含有単量体は、アミノプラスチック樹脂の硬化反応促進効果を有し、さらに塗膜密着性を高めるために配合され、その使用量は(a), (b), (c) からなる全重合性単量体成分中 0.1~10重量%が必要であり、好ましくは1~8重量%である。0.1重量%より少ないと、硬化促進効果および塗膜密着性が発現せず、10重量%より多いと重合中にゲル化したり、重合後にアミノプラスチック樹脂と混合し被覆用樹脂組成物とした時の安定性が悪くなる。

【0015】リン酸基以外の酸性官能基を有する単量体は、単量体成分中0.9~15重量%が好ましく、より好ましい使用量は5~15重量%であり、前記のカルボキシル基もしくはスルホン酸基を有する単量体のうち1種または2種以上使用することができる。これらのカルボキシル基もしくはスルホン酸基含有単量体が0.9重量%より少ないと金属に対する密着性が不足し、15重量%を超えて使用すると、塗膜の耐水性が悪化するため好ましくない。

【0016】水酸基含有重合性単量体(b)としては、例えば、ヒドロキシエチル(メタ)アクリレート、ヒドロキシプロピル(メタ)アクリレート、カプロラクトン変性ヒドロキシ(メタ)アクリレート(例えば、ダイセル化学工業社製; プラセルF M)、フタル酸とプロピレングリコールから得られるポリエステルジオールのモノ(メタ)アクリレート等が挙げられる。

【0017】上記水酸基含有単量体(b)の使用量は、単量体成分全量中0~20重量%、より好ましくは0~10重量%である。水酸基は、アミノプラスチック樹脂との硬化反応に必要であるが、重合時に必須的に存在する前記エポキシ樹脂のエポキシ基が開環することによって水酸基が生成することもあり0~20重量%である。20重量%を超えると架橋密度が上がり過ぎるため、密着性、可撓性が悪くなる。

【0018】その他の重合性単量体(c)としては、メチル(メタ)アクリレート、エチル(メタ)アクリレート、プロピル(メタ)アクリレート、イソプロピル(メタ)アクリレート、ブチル(メタ)アクリレート、イソブチル(メタ)アクリレート、第3級ブチル(メタ)アクリレート、2-エチルヘキシル(メタ)アクリレート、ラウリル(メタ)アクリレート、ステアリル(メタ)アクリレート、シクロヘキシル(メタ)アクリレー

ト、メチルシクロヘキシル(メタ)アクリレート、第3級ブチルシクロヘキシル(メタ)アクリレート等の(メタ)アクリル酸アルキルエステル; グリシジル(メタ)アクリレート等のエポキシ基含有重合性単量体; (メタ)アクリルアミド、メチルアルコキシ(メタ)アクリルアミド、N,N'-ジメチルアミノエチル(メタ)アクリレート、ビニルピリジン、ビニルイミダゾール等の窒素含有重合性単量体; 塩化ビニル、塩化ビニリデン等のハロゲン含有重合性単量体; スチレン、 α -メチルスチレン、ビニルトルエン等の芳香族重合性単量体; 酢酸ビニル等のビニルエステル; ビニルエーテル; (メタ)アクリロニトリル等の重合性シアニ化合物; 2,4-ジヒドロキシベンゾフェノンまたは2,2',4-トリヒドロキシベンゾフェノンとグリシジル(メタ)アクリレートを反応して得られる2-ヒドロキシ-4-[3-(メタ)アクリルオキシ-2-ヒドロキシプロポキシ]ベンゾフェノン、2,2'-ジヒドロキシ-4-[3-(メタ)アクリルオキシ-2-ヒドロキシプロポキシ]ベンゾフェノン等の重合性紫外線吸収性単量体等が挙げられ、これらの群から選ばれる1種または2種以上を用いることができる。

【0019】その他の単量体(c)は、全重合性単量体成分中55~99重量%使用され、塗膜物性を決定する主成分である。硬度や耐水性の面からはスチレンを単量体全成分中10~40重量%使用するのが好ましい。

【0020】本発明においては、前記芳香族エポキシ樹脂の存在下に、前記(a)~(c)の単量体成分を重合させるのであるが、重合法としては公知の溶液重合法を採用することができる。溶液重合法を採用する際に使用できる溶剤としては、トルエン、キシレン等の芳香族炭化水素類; 酢酸エチル、酢酸ブチル等の酢酸エステル類; メチルエチルケトン、メチルイソブチルケトン等のケトン類; イソプロパノール、n-ブタノール、iso-ブタノール等の脂肪族アルコール類; エチレングリコールモノメチルエーテル、エチレングリコールモノエチルエーテル、ジエチレングリコールモノエチルエーテル等のアルキレングリコールモノアルキルエーテル類等を挙げることができる。

【0021】これらの溶剤は1種または2種以上を使用することができるが、その使用量は重合性単量体成分100重量部に対して25部~100重量部が適している。また、リン酸基含有単量体が存在していると重合中にゲル化し易いが、n-ブタノール等の脂肪族アルコール類が溶剤中に含まれているとゲル化が起こらないことが判明したので、重合性単量体100重量部に対して10重量部以上は脂肪族アルコールとすることが好ましい。

【0022】重合開始剤としては、アゾビスイソブチロニトリル、ベンゾイルパーオキサイド、ジ第3級ブチルパーオキサイド等のラジカル重合開始剤を挙げることができる。これらの重合開始剤は、重合性単量体成分の総

5

量に対して0.1~10重量%の範囲で使用される。反応温度は室温から200℃、好ましくは40~140℃の範囲である。また重合反応を行なう際に、分子量を調節する目的で、ラウリルメルカプタン、2-メルカプトエタノール、四塩化炭素、四臭化炭素等の連鎖移動剤や調節剤を用いてもよい。

【0023】以上の重合によって芳香族エポキシ樹脂とリン酸基、酸性官能基、水酸基の導入されたアクリル系共重合体がリン酸基部分でエポキシ基と反応しグラフトして一体化した変性アクリル樹脂からなる被覆用樹脂が合成される。この被覆用樹脂の数平均分子量は3000~50000が適している。数平均分子量が3000より小さいと、硬化後の塗膜の物性が劣るため好ましくなく、50000より大きい場合には樹脂の粘度が高くなるため塗料として取り扱いに不便を生じる。

【0024】本発明で製造される被覆用樹脂は、単独で使用することも可能だが、アミノプラスト樹脂を混合して使用することが好ましい。またアミノプラスト樹脂としては、例えば、アルキルエーテル化メラミン樹脂、アルキルエーテル化ベンゾグアナミン樹脂、アルキルエーテル化尿素樹脂等を挙げることができ、これらの1種または2種以上の混合物を使用できる。アミノプラスト樹脂の使用量は、被覆用樹脂100重量部に対して5~70重量部の割合で配合するのが良い。アミノプラスト樹脂の使用量が5重量部未満では、架橋が不十分で耐久性のある塗膜を得るのが困難となり、耐水性、塗膜硬度が低下する。また70重量部を超えて用いると可撓性が劣るため好ましくない。

【0025】本発明の被覆用樹脂は、反応を促進させるための硬化触媒、有機溶剤、充填剤、レベリング剤、分散剤、可塑剤、安定剤、染料、顔料等の各種塗料用添加剤を適宜配合して使用することができる。

【0026】本発明の被覆用樹脂に使用できる顔料としては、例えば、無機顔料では、酸化チタン、三酸化アンチモン、亜鉛華、リトボン、鉛白等の白色顔料、カーボンブラック、黄鉛、モリブデン赤、ベンガラ、黄色酸化鉄、黄華等の着色顔料、また有機顔料ではベンジジン、ハンザイエロー等のアゾ化合物やフタロシアニンブルー等のフタロシアニン類等を挙げることができ、これらの1種または2種以上を用いることができる。またこれらの顔料は、塗膜の耐候性を低下させることのないように、耐候性の良好な顔料を選択することが推奨され、例えば、白色顔料である酸化チタンとしては、アナターズ型の酸化チタンを用いるより、ルチル型の酸化チタンを用いる方が塗膜の耐候性という面では良い結果が得られ、さらに硫酸法酸化チタンより塩素法酸化チタンの方が長期耐候性を発現させる上で好ましい。

【0027】

【発明の効果】本発明の被覆用樹脂は、芳香族エポキシ樹脂がリン酸基、その他の酸性官能基および所望により

6

水酸基を有するアクリル系共重合体と反応して一体化した樹脂となっているので、保存安定性に優れており、さらにリン酸基の導入によって硬化時間が短かくても、密着性、硬度、耐水性、加工性等に優れた塗膜を形成し得るものである。

【0028】

【実施例】以下、実施例を挙げて本発明を具体的に説明するが、本発明はこれらの実施例に限定されるものではない。なお「%」および「部」は、それぞれ「重量%」および「重量部」を示す。

【0029】製造例1

温度計、攪拌機、窒素ガス導入管、還流冷却器および滴下槽を備えた4つ口フラスコに、ブチルセロソルブ26部、n-ブタノール17部、エビコート1001（油化シエルエポキシ社製；エポキシ当量450~500）を25部仕込み、窒素ガスを導入しながら攪拌下で90℃に保ち、滴下槽からアクリロイルオキシエチルアシッドフォスフェート4部、メタクリル酸6部、ヒドロキシエチルアクリレート5部、スチレン25部、エチルアクリレート27部、n-ブチルアクリレート7.8部、ジメチルアミノエチルメタクリレート0.2部、アゾビスイソブチロニトリル3部の混合物を4時間にわたって滴下した。その後90℃で2時間反応させた後、さらにアゾビスイソブチロニトリル0.3部添加し4時間維持して反応を終了した。ブチルセロソルブ24部を添加し、固形分60%、数平均分子量5000、粘度15000cps（25℃；B型粘度計、以下同じ）、酸価30の被覆用樹脂A1を得た。

【0030】製造例2

温度計、攪拌機、窒素ガス導入管、還流冷却器および滴下槽を備えた4つ口フラスコに、ブチルセロソルブ50部、n-ブタノール17部、エビコート1004（油化シエルエポキシ社製；エポキシ当量900~1000）15部仕込み、窒素ガスを導入しながら攪拌下で90℃に保ち、滴下槽からメタクリロイルオキシエチルアシッドフォスフェート2部、メタクリル酸8部、ヒドロキシエチルアクリレート7部、スチレン30部、エチルアクリレート30部、n-ブチルアクリレート8部、アゾビスイソブチロニトリル5部の混合物を4時間にわたって滴下した。その後90℃で2時間反応させた後、さらにアゾビスイソブチロニトリル0.5部添加し3時間維持して反応を終了した。固形分60%、数平均分子量4000、粘度16000cps、酸価35の被覆用樹脂A2を得た。

【0031】製造例3

温度計、攪拌機、窒素ガス導入管、還流冷却器および滴下槽を備えた4つ口フラスコに、ブチルセロソルブ35部、n-ブタノール8部、エビコート1001を20部、アクリロイルオキシエチルアシッドフォスフェート4部を仕込み、窒素ガスを導入しながら攪拌下90℃に保ち、滴下槽からメタクリル酸8部、ヒドロキシエチルアクリレート5部、スチレン25部、エチルアクリレート30部、

n-ブチルアクリレート 8部、アゾビスイソブチロニトリル 3部の混合物を4時間にわたって滴下した。その後90℃で2時間反応させた後、さらにアゾビスイソブチロニトリル 0.3部添加し4時間維持して反応を終了した。ブチルセロソルブ24部を添加し、固形分60%、数平均分子量4000、粘度18000cps、酸価40の被覆用樹脂A3を得た。

【0032】製造例4

エピコート1001をエピコート828（油化シェルエポキシ社製；エポキシ当量 182~194）にかえた以外は製造例3と同様にして、固形分60%、数平均分子量3500、粘度11000cps、酸価35の被覆用樹脂A4を得た。

【0033】比較製造例1

エピコート1001を使用しなかった以外は製造例3と全く同様に重合を行ない、固形分60%、数平均分子量12000、粘度15000cps、酸価45の被覆用樹脂B1を得た。

【0034】比較製造例2

比較製造例1で得られた樹脂B1にエピコート1001を20重量%使用しなかった以外は製造例3と全く同様に重合を行ない、固形分60%、数平均分子量12000、粘度15000cps、酸価45の被覆用樹脂B2を得た。

【0035】比較製造例3

アクリロイルオキシエチルアシッドフォスフェートを使用しなかった以外は製造例3と全く同様に重合を行ない、固形分60%、数平均分子量3500、粘度15000cps、酸価35の被覆用樹脂B3を得た。

【0036】実施例1

被覆用樹脂A160.5部、ヘキサメトキシメラミン（三井東圧化学社製；サイメル303；固形分 100%）15.5部、アミンブロックしたバタトルエンスルホン酸0.2部、ブチルセロソルブ23.8部を混合し塗料組成物を作成した。

【0037】実施例2~4および比較例1~3

表1に示した様に被覆用樹脂を変化させ、実施例1と同様に塗料組成物を作成した。

【0038】実施例5~6

表1に示した被覆用樹脂32.0部とメチルエーテル化メチロールメラミン（三井東圧化学社製；サイメル370；固形分88%）9.4部、酸化チタン27.5部、アミンブロックしたバタトルエンスルホン酸 0.2部、ブチルセロソルブ30.9部を混合し塗料組成物を作成した。

【0039】実施例で得られた塗料組成物を、厚さ 0.3 mmのリン酸亜鉛処理鋼板に乾燥後の塗膜厚が15~20μmになる様にロールを用いて塗工し、230℃で1分間焼付けを行なった。焼付け後の塗膜を以下の項目について評価し、結果を表1に併記した。

【0040】〈塗料安定性〉50℃で1か月保存した時の増粘および分離状態を目視観察した。

〈耐水性〉常温で水中浸漬7日後の塗膜の白化、プリスターの状態を目視で判定した。

〈耐沸水性〉沸騰水に2時間浸漬後の塗膜の白化、プリスターの状態を目視で判定した。

【0041】〈加工性〉試験片を 180° 折り曲げ（OT）、屈曲部のクラック、剥離状態を目視で判定した。

〈耐衝撃性〉デュボン1/2 インチ、500 gの荷重、距離50 cmで行ない、塗膜のクラック、剥離状態を目視で判定した。

〈鉛筆硬度〉JIS S 6006 に規定される鉛筆を用い、JIS K 5400 に従って測定した。

【0042】〈密着性〉1 cm² の中に1 mm幅の 100 個のます目を作り、テープ剥離後の残った目の数を示した。

〈耐塩水噴霧性〉塗装面以外をシールし、塗膜面側に素地に塗するまでカットした後、塩水噴霧試験機に入れ、500時間後に取り出し、テープ剥離を行なった。片側剥離幅1 mm以下を○、1~3 mmを△、3 mm以上を×とした。

【0043】

【表1】

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| | 実 施 例 | | | | | | 比 較 例 | | |
|------------------------------|-------|-----|-----|-----|-----|-----|-------|-----|----|
| | 1 | 2 | 3 | 4 | 5 | 6 | 1 | 2 | 3 |
| 被覆用樹脂A1 | 70 | 70 | | | | 70 | | | |
| " A2 | | | | | 70 | | 70 | 70 | 70 |
| " A3 | | | | | | | | | |
| " A4 | | | | | | | | | |
| " B1 | | | | | | | | | |
| " B2 | | | | | | | | | |
| " B3 | | | | | | | | | |
| ヘキサメトキシ メチロール メチル化メラミン | 30 | 30 | 30 | 30 | 30 | 30 | 30 | 30 | 30 |
| 塗料安定性 | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ |
| 耐水性 | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ |
| 耐沸水性 | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ |
| 加工性 | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ |
| 耐衝撃性 | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ |
| 鉛筆硬度 | 5H | 5H | 5H | 4H | 5H | 5H | 5H | 3H | 3H |
| 密着性 | 100 | 100 | 100 | 100 | 100 | 100 | 70 | 100 | 75 |
| 耐塩水噴霧性 | ○ | ○ | ○ | ○ | ○ | ○ | △ | ○ | △ |

被覆用樹脂とメラミンの配合比は固形分換算である。